



Geochemical features of re-deposited organic matter occurring in fluvio-glacial sediments in the Racibórz region (Poland): A case study

Monika Fabiańska*, Konrad Miotliński, Andrzej Kowalczyk

Faculty of Earth Sciences, University of Silesia, 41-200 Sosnowiec, Będzińska Street 60, Poland

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ABSTRACT

The erosion of rocks rich in organic matter typically leads to the complete mineralization of the organic material. However, in some cases, it is re-deposited to become a part of sediments once more. This process should be considered to be a part of global carbon cycle, possibly much more significant than assumed to-date. The research presented here aims to characterize re-worked organic matter occurring in post-glacial sediments of southern part of Poland, in the Oder river valley (the Racibórz town region, Miocene, Pleistocene and Holocene age). Organic substances extracted from the sediments originated from organic matter that had resided in rocks eroded by glaciers. Sediments were sampled in two boreholes which sediments were correlated. Sediments were extracted and extracts analyzed with gas chromatography-mass spectrometry (GC-MS) to assess distributions of biomarker groups. Organic matter of selected samples was pre-concentrated and analyzed with Py/GC-MS. In the extracts several biomarker parameters of source/environment and thermal maturity were calculated. Organic substances in the investigated sediments come from variable re-deposited organic matter occurring in rocks eroded by glaciers. Three main parent types of re-deposited organic material are identified showing variable geochemical features: 1) organic matter of recent or almost recent age being the source of polar labile compounds; probably formed *in situ*, 2) re-deposited organic matter of the middle diagenesis showing features similar to lignites (huminites reflectance $R_f \sim 0.25\text{--}0.35\%$) deriving from angiosperm remains, mainly monocotyledons and to the lower extend also deciduous trees, 3) re-deposited organic matter at the middle catagenesis ($R_f \sim 0.65\text{--}0.75\%$) being the source of most of aromatic hydrocarbons and biomarkers such as steranes, hopanes of the more thermally advanced distribution type. Its geochemical properties and assumed directions of sediment transport indicate bituminous coals of Upper Silesian Coal Basin together with coaly shales as a possible source of this organic matter. Such mixed origin of organic matter caused large discrepancies in values of thermal maturity parameters depending on input from the particular sources and occurrence both geochemical biomarkers and their biochemical precursors in the same samples.

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1. Introduction

1.1. Re-deposited organic matter

It has been calculated that ca 0.1 Gt of organic carbon is released annually from carbonates and shales by weathering to participate in the global carbon cycle once again (Di-Giovanni *et al.*, 2002). Subsequently, it can be oxidised to carbon dioxide or recycled, mainly in various biological processes (Tissot and Welte, 1984). Generally it is considered that only a small amount of the released organic matter is re-deposited in sediments as it is prone to extensive alteration and

destruction by biological and physicochemical processes as it passes through the hydrosphere. However, in some cases it can be re-deposited to become a sediment component once again. A significant amount of weathered organic matter may end up in rivers (e.g. Meybeck, 1987). This re-deposition should be considered an important part of the global carbon cycle, possibly much more significant than is generally assumed.

Weathering, erosion and re-deposition cause significant changes in the geochemical features of organic matter. To-date, the nature of these alterations has not been well defined. However, there are several examples of investigations of the geochemical features of re-deposited organic matter in the literature. Most concern glacial sediments deposited recently or in the past (McDonald *et al.*, 1991; Villanueva *et al.*, 1997; Di-Giovanni *et al.*, 1999).

In most such cases, the organic matter is more thermally mature than it should be based on the age and geological history of sediments in which it occurs. For example, McDonald *et al.* (1991) investigating

* Corresponding author. Tel.: +48 32 291 83 81, +48 32 291 89 01-9x244/228(Central); fax: +48 32 291 58 65.

E-mail addresses: mfabians@wnoz.us.edu.pl, monika.fabianska@neostrada.pl (M. Fabiańska).

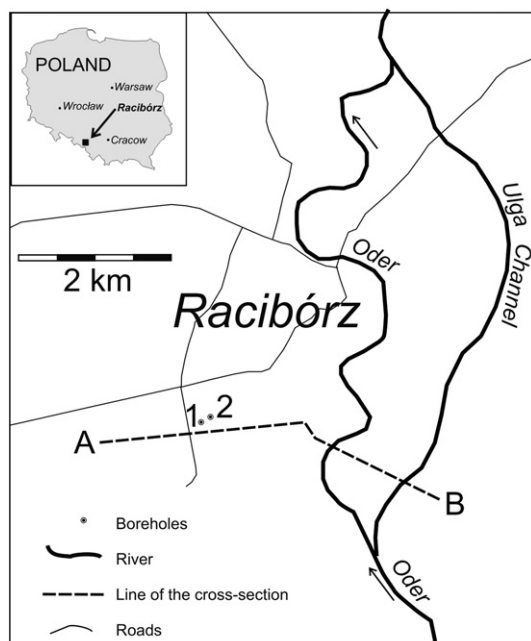


Fig. 1. Sketch map of the area investigated. The map of Poland shows the locality of Racibórz and the major Polish cities.

glacial and Cretaceous sediments in Antarctica, found that organic matter present in Quaternary–Miocene sediments age to be mature (catagenesis) whereas organic matter in underlying middle Eocene to early Oligocene sediments to be immature. Based on biomarker-, optical- and Rock Eval Analysis data, this reversal in maturities was deemed to reflect erosion and re-deposition that recycled organic matter (McDonald et al., 1991). Similarly, over-mature organic matter in glacial Cainozoic sediments in the Norwegian Sea reflects glacial erosion of Mesozoic sediments of the Scandinavian- and Barents Sea shelves that had begun in the early Pliocene (Holemann and Henrich, 1994). Finally, re-deposited organic matter in North-Atlantic sediments, largely transported as ice-rafted debris (Villanueva et al., 1997), is severely altered with high mixed contents of unresolved compounds.

Despite differences in biological origin, age and maturity, loss of reactivity (Hartog et al., 2004) and lower contents of extractable organic matter, both caused by partial oxidation, are common features of re-worked organic matter. As a result of re-working related to processes such as defunctionalisation, carbonization and oxidation, organic matter often acquires a refractory character (Di-Giovanni et al., 1999). Generally, organic matter of terrestrial origin seems to survive such conditions better than do other types of organic matter more susceptible to destruction (Holemann and Henrich, 1994; Di-Giovanni et al., 1999).

Since the most favorable conditions for organic matter re-deposition should include low temperature, a relatively high erosion

rate and rapid deposition in sediments preventing biodegradation and oxidation, glacial sediments are an obvious focus for investigation. These conditions apply in recent glacial sediments (Fabiańska et al., 2006). The first aim of the research presented here was to establish whether it is possible to apply geochemical biomarker analysis to characterize organic material re-deposited in glacial sediments despite its extensive re-working, mixed origin and generally low contents. The second aim was to differentiate sources of organic matter using procedures applied in oil–oil and oil–kerogen correlations and to identify probable sources of organic matter.

1.2. Geological background

The area investigated is located in the Oder river valley near Racibórz town in southern Poland (Fig. 1). During the Quaternary, the area of Poland experienced a number of glaciation periods separated by interglacials. The site studied lies at the southernmost limit of the area covered by the ice. The valley is filled with a thick (<80 m) sequence of sandy and gravely outwash deposits (Fig. 2). These deposits are underlain by a thick (~200 m) sequence of Miocene deposits covered by a thin (up to a few meters) layer of Holocene age (Kotlicka, 1978). Within the Middle Miocene deposits, there are terrigenous clays with thin intercalations of lignite (Alexandrowicz, 1997). The western boundary of the Upper Silesian Coal Basin, one of the most important hard coal basins in the European Variscides, is located ca 15 km to the east of the study site.

The Lower Pleistocene unit (<50 m thick) comprises unsorted sands and gravels with small pebbles deposited in braided rivers. These sediments, which only occur in depressions within the Miocene deposits, do not crop out to the surface and have been seen only in borehole material. The alluvium predominantly consists of variably altered fragments of sandstones eroded from the Carpathians and quartz originating from the Sudetes (Kotlicka, 1978). Grain size ranges from 0.2 mm to 10 cm. The gravel (>2 mm) fraction represents 26–50% of the series. Subsamples from the sandy fraction (0.05–2 mm) represent <55% of the series (Kotlicka, 1978). Some of the underlying Miocene, including fragments of dark gray clay, has been re-worked into the Lower Pleistocene deposits.

During the Middle Pleistocene, both glacial and limnoglacial deposits formed. However, most glacial deposits in the valley were eroded during the subsequent interglacial periods. Nevertheless, glacial deposits occur in the upland areas and reach a thickness of <40 m. These deposits comprise dark grey till with erratic boulders. The glacial till is commonly interbedded with a gravel layer <10 m thick. Gravels and small pebbles in this layer on average constitute 75% of the whole. The Middle Pleistocene limnoglacial deposits only occur within the buried valley and reach 40 m in thickness (Kotlicka, 1978). Particle sizes range from clay to boulders though silt- to medium sand particles predominate. The main constituents of the Middle Pleistocene deposits are well-rounded quartz grains, quartzite and greywacke sandstones. Strongly weathered fragments of porphyries, gneisses and granites of Scandinavian origin are also apparent (Kotlicka, 1978).

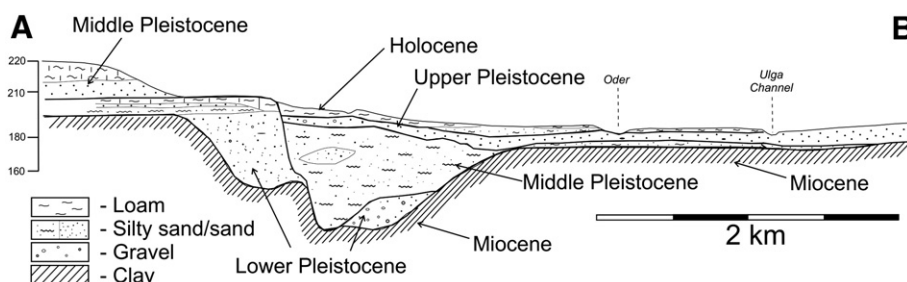


Fig. 2. Geological cross-section along the line A–B through the Racibórz region (Poland) (after Kotlicka, 1978).

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